

WATER TRANSPORT IN AIR FORCE ORGANIC COATINGS

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ABSTRACT

Current Air Force coatings include urethane topcoat-chromate pigmented epoxy primer systems with the topcoat functioning as a barrier against the environment and the chromate primer providing adhesion between the topcoat and the substrate as well as passivation of the AA 2024-T3 substrate. Experimental results demonstrating the water uptake and water loss associated with a non-pigment epoxy coating and the Air Force chromate pigmented primer are presented. The experimental procedure involved exposure of the coatings to NaCl and room temperature ionic liquid media. The latter allowed monitoring of the coating being dried by the hydrophilic and conductive ionic liquid. In-situ single-frequency impedance measurements were used to monitor the evolution of capacitance changes associated with water uptake/loss while electrochemical impedance spectroscopic measurements were used to determine the coating properties after the immersion period. The capacitance evolution associated with the chromate primer was anomalous with a 50 factor increase during immersion in NaCl as compared to less than a 2 factor increase for the non-pigmented epoxy. Large changes in coating capacitance have been reported for organic coatings during aqueous immersion, however there has been limited effort to determine this anomalous result. The electrochemical and gravimetric results presented were used to propose the hypothesis that the large increase in capacitance of the chromate primers was due to the ingress of an electrolytic species. This hypothesis represents a work in progress upon which more sophisticated versions will be developed.

Keywords: diffusion coefficient, single-frequency impedance, chromate primer

INTRODUCTION

The corrosion of metallic structures is mitigated by the protection provided by organic coatings. Two-layered coatings are designed to reduce the transport of water, ions, and oxygen from the environment to the substrate. The topcoat acts as a barrier against the environment whereas the basecoat/primer provides adhesion to the substrate and additional protection such as galvanic (zinc rich primers) or passivation of the substrate (chromate primers). The water transport property of a defect free coating is determined by diffusion with the diffusion coefficients of water ingress D_{in} and egress D_{out} being important parameters. Salt spray test and the Prohesion test are standard tests that are used to determine a coating's protective ability and both involve moisture exposure.

The importance of water uptake of organic coatings is well covered in literature for single-layered^{1,2,3} and two-layered coatings.^{4,5,6} In the literature the evolution of water uptake for an individual coating layer is assumed to be consistent with Fick's second law for the concentration distribution of water

$$\frac{\partial c(z,t)}{\partial t} = D \frac{\partial^2 c(z,t)}{\partial z^2} \quad (1)$$

where c and D are the concentration and diffusion coefficient of water, respectively. The independent variables are position z , measured from a reference point, and time t . Gravimetric measurements have been used to calculate the diffusion coefficient D_{out} associated with the desorption of water^{1-3,7-10} using a solution to Fick's second law for water transport

$$\frac{M_t}{M_s} = 1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp\left(\frac{-(2n+1)^2 D \pi^2 t}{4L^2}\right) \quad (2)$$

where M_t and M_s represent the mass of water absorbed at time t and at saturation, respectively, and L is the coating thickness.¹¹ This solution is limited to the condition that D is independent of c and is applicable to a system desorbing water as well as absorbing water.¹¹ The term on the left-hand-side of Eq. (2) represents the degree of saturation of the coating. An expression that is used to calculate D from gravimetric results is a short time approximate solution for Eq. (2)

$$\frac{M_t}{M_s} = \sqrt{\frac{4Dt}{L^2 \pi}} \quad (3)$$

which involves replacing the summation by an integration.¹¹

The capacitance evolution of an organic coating has been used to calculate D_{in} by relating the volumetric changes associated with water absorption with the expression for mass changes.^{3,7,12-14} The

capacitance of a coating changes during water ingress because there is a change in the dielectric property of the coating due to the large difference between the relative dielectrics of water and the polymeric material of the coating. The coating capacitance during wetting can be monitored using the electrochemical impedance spectroscopy (EIS) response of a high frequency signal applied to the coating. A relationship for the volume fraction occupied by water ϕ_t at a time t is given by

$$\phi_t = \frac{\ln(C_t / C_0)}{\ln \varepsilon_w} \quad (4)$$

where C_0 and C_t represent the coating capacitance at $t=0$ and at any time t , respectively, and ε_w represents the permittivity of water.¹ The ratio of volume fraction at time t to that at saturation ϕ_s is an expression for the degree of saturation and is given by

$$\frac{\phi_t}{\phi_s} = \frac{\ln(C_t / C_0)}{\ln(C_s / C_0)} \quad (5)$$

where C_s represent the coating capacitance at saturation (1,2). Combination of Eqs. (2) and (5) and Eqs. (3) and (5) yield expressions for calculating the value of D from capacitance measurements. The expression on the right-hand-side of Eq. (5) represents a dimensionless capacitance. Other expressions with a dimensionless capacitance on the right-hand-side are

$$\frac{\phi_t}{\phi_s} = \frac{C_t - C_o}{C_s - C_o} \quad (6)$$

and

$$\frac{M_t}{M_s} = \frac{C_t - C_o}{C_s - C_o} \left(\frac{C_s}{C_t} \right) \quad (7)$$

The right-hand-side of Eq. (6) is referred to as a discrete model while that of Eq. (7) is referred to as the continuous model in literature.³ The right-hand-side of Eq. (5) is used to relax the assumption that the degree of water saturated condition is $\phi_s \ll 1$ that is associated with the discrete model. The discrete model is based on the assumption that the concentration of water is uniform in a coating during ingress of water and the continuous model is based on the assumption that the profile for the concentration of water is consistent with Fick's second law.

During desorption of water the coating capacitance also changes. The monitoring of the capacitance changes by EIS would require an electrochemical contact to the coating during the drying process. Reports by our group and the work presented in this effort have demonstrated the methodology

whereby room temperature ionic liquids (RTILs) can be used to monitor the capacitance changes of a coating during the drying process.^{13,15-19} RTILs are salts that have melting points close to or below room temperature with ionic conductivities over 0.01 Scm^{-1} at room temperature²⁰ that have been used for electrodeposition of metals and semiconductors, and corrosion studies of metals.^{21,22} The conductivity allows RTILs to provide a non-aqueous medium for electrochemical measurements while a hydrophilic RTIL also provides a medium that removes water from an organic coating. It has been reported that the capacitance evolutions associated with the exposure of an epoxy coating on Aluminum Alloy (AA) 2024-T3 to immersion in 0.05 M NaCl and a hydrophilic RTIL were both consistent with Fick's second law.¹⁵ The values of D associated with the ingress and egress of water were reported to be similar. This result demonstrated the applicability of a hydrophilic RTIL as a non-aqueous media for desorption studies.

Experimental results are presented for a non-pigment epoxy single layer coating and a standard Air Force primer that is an epoxy pigmented with a chromate compound. The coatings were subjected to alternate immersion in 0.05 M NaCl and a hydrophilic RTIL during which electrochemical measurements were made. The capacitance evolution associated with the chromate primer was strikingly anomalous where there was a 50 factor increase during immersion in NaCl while less than a 2 factor increase for the un-pigmented epoxy. The large change in capacitance has been reported for organic coatings during aqueous immersion, however there has been limited effort to determine this anomalous result.²³ The electrochemical and gravimetric results presented were used to propose a hypothesis for the anomalous result in coating capacitance. This hypothesis represents a work in progress upon which more sophisticated versions will be developed.

EXPERIMENTAL PROCEDURE

Single-layer non-pigmented epoxy and a chromate-pigmented primer were the coatings used in the experiments. The substrate was AA 2024-T3 (UNS A92024) which was washed in deionized water and cleaned with hexane before application of the coating. The epoxy was made by mixing Epon Resin 828 RS and Epicure 3115-X-70 curing agent in equal volumes with a 2-butanone (99%) solvent which represented 25 vol. % of the total mixture volume. The supplier for the resin and curing agent was Resolution Performance Products of Houston TX, and for the 2-butanone solvent was Sigma Aldrich. The 5 by 8 inches AA 2024-T3 panels were supplied by Q-Panel Lab Products of Cleveland OH. The curing stage consisted of 6 hours at 60 °C followed by at least 48 hours at room temperature. The chromate pigmented epoxy primer was Deft 02-Y-40, MIL-P-23377G Type I Class C and was applied on the AA 2004-T3 panels that were pretreated by a phosphate alcohol solution. The epoxy and chromate primer were applied to the panels using a compressed air spray-gun.

Immersion of a coated panel was achieved using a clamped glass cylinder with an O-ring insert with the cylinder exposing a 7.07 cm^2 of the coating to the immersing electrolyte. The area on the coated panel for testing was marked after visual inspection for defects and thickness measurements for uniformity. The reported thickness of a sample area was the average of 13 measurements with an Elcometer 345 NS, supplied by Elcometer Instruments Ltd. of Rochester Hills, MI. The cylinder was removed and the sample wiped with a Kimwipes[®] to remove residual electrolyte on the coating between the wetting and drying stages. A clean cylinder and O-ring was then clamped to the sample. For the drying stage of the NaCl-RTIL experiment a clean counter electrode was used each time. The thickness of the epoxy coating was 100 μm and for the chromate primers were 43 ± 4 , 37 ± 5 , and $45 \pm 2 \mu\text{m}$ which were designated as P1, P2, and P3 respectively.

A two-electrode configuration was used for electrochemical measurements where the substrate was the working electrode and a Pt mesh was the counter/reference electrode. The Pt mesh was placed approximately 5 mm from the surface of the coating and sufficient electrolyte was used to totally immerse it. Instrumentation for electrochemical measurements were a Gamry PCI4/300™ Potentiostat that was controlled by Gamry Framework Version 4.21/EIS 300 software, with Gamry Instruments, Inc. of Willow Grove, PA the supplier. A single frequency, electrochemical impedance measurement was conducted where the impedance at an applied single frequency of 10 kHz was monitored for an immersed coating every 120 s for a period of time. Conventional EIS measurement were also conducted where the impedance associated with applied frequencies over a 100 kHz to 0.01 Hz range were measured at an acquisition rate of 10 points per decade. A 15 mV amplitude perturbation potential was employed for both measurements.

The epoxy coating was characterized by alternate immersion for 24 hours in 0.05 M NaCl and RTIL. The hydrophilic RTIL was 1-Butyl-1-methylpyrrolidinium trifluoromethanesulfonate (C₁₀H₂₀F₃NO₃S) which was supplied by EMD Chemicals, Inc. of Gibbstown NJ. Immersions in the 0.05 M NaCl and RTIL media represented wetting and drying stages, respectively. A single frequency measurement was performed during the stages to monitor the capacitance changes due to water ingress for wetting and water egress for drying. After the single-frequency measurement, a conventional EIS measurement was conducted to obtain the electrochemical behavior of the coating in the electrolyte.

The chromate primer was characterized similar to the epoxy coating except that the immersion period in the NaCl and RTIL media was 4 to 7 days. The chromate primer was also characterized by alternating between immersion in the NaCl medium and drying in a dessicator. A single-frequency measurement and a conventional EIS measurement were made during the wetting stage and at the end of the wetting stage, respectively, in NaCl medium. No electrochemical measurements were made during the drying period in the dessicator.

Gravimetric measurements were made using a ThermoGravimetric Analysis (TGA-Q500) instrument. Chromate primer samples of approximately 5 mm² in area were allowed to saturate with water by immersion in 0.05 M NaCl for 4 days before gravimetric measurements. Water on the surface of a sample was removed with a paper tissue before the sample was placed on a TGA pan. The gravimetric measurement involved a temperature ramp at 20 °C/min. to a 35 °C temperature after which the temperature was held there for several hours while the weight loss was monitored.

RESULTS

The capacitance data $C(t)$ was calculated using

$$C = (-\omega Z_j)^{-1} \quad [6]$$

where the angular frequency ω and the imaginary part of the impedance Z_j was associated with the data obtained at the single frequency of 10 kHz. The experimental capacitance evolution results were coupled with Eq. (4) to yield a calculated water uptake evolution.

The characteristic capacitance evolution for an organic coating undergoing water absorption is based on the solution to Fick's second law Eq. (1) in which the evolution with respect to the square root

of time includes a linear increase in capacitance followed by an asymptotic approach to a steady value.¹⁵ Fick's second law is also applicable to desorption of water, therefore, the evolution associated with desorption of water would include a linear decrease in capacitance followed by an asymptotic approach to a steady value.¹⁵ The asymptotic steady value for absorption indicating a saturated coating while the asymptotic steady value for desorption indicating when there is negligible further desorption of water from the coating.

Epoxy Coating

The evolutions of the calculated capacitance associated with wetting by 0.05 M NaCl and drying by RTIL are presented for the single-layered non-pigmented epoxy coating in Figure 1. It was observed that upon immersion in the aqueous NaCl, a wetting stage, the capacitance increased and approached an asymptotic value. Immersion in the RTIL, a drying stage, resulted in the exponential decrease in capacitance toward an asymptotic value. There was an increase in capacitance by a 1.5 factor, approximately, during the wetting stages and a decrease by a 1.5 factor, approximately, during the drying stages. The time for the epoxy to become saturated was approximately 4 days and likewise the time for the drying process to come to completion in the RTIL medium was approximately 4 days. The capacitance change associated with the first wetting and drying stages are shown as functions of $t^{0.5}$ in Figure 1. The trend with $t^{0.5}$ indicated that the ingress of water during the wetting stage and the egress of water during the drying stage were consistent with Fick's second law.

The water uptake evolution associated with the first wetting and drying stages of the epoxy coating are shown in Figure 2. The saturated condition under NaCl immersion was 6.6 vol. % with a dry condition of -6.0 vol. % associated with the RTIL immersion. These results demonstrated that the water taken up during the wetting condition was removed during the drying condition. Ideally, the magnitude of the water loss and water taken up should be equal and the observed difference was attributed to the approximation of the initial capacitance of the coating and the experimental errors introduced by films of NaCl or RTIL that remain during the alteration between conditions.

The Bode modulus plot of the EIS data obtained at the ends of the immersion periods in NaCl and RTIL are shown in Figure 2. The $|Z|$ data under NaCl immersion had a slope of -1 for frequencies greater than 100 Hz. There was a transition to a plateau region and a plateau region for frequencies less than 100 Hz. The slope of -1 was indicative of capacitance behavior at high frequencies and the plateau region indicated that there was resistance associated with the coating at the low frequency end of the spectrum. The $|Z|$ data under the RTIL immersion had a slope of approximately -1 over the frequency range applied. The absence of a plateau region indicated that the resistance behavior of the epoxy was not attained in the frequency range used and it was therefore greater than the $5 \times 10^{11} \Omega \text{ cm}^2$, the $|Z|$ value associated with the 0.01 Hz frequency. This result indicated that the conductive 0.05 M NaCl was removed from the epoxy coating by the RTIL.

The capacitance data for the epoxy coating was cast into dimensionless form using the discrete model and continuous model functions. The evolutions of these functions are shown in Figure 3 for the data during the immersion in NaCl and RTIL. The slope of the linear portion of a plot for the NaCl medium was used to calculate D_{in} and of the plot for the RTIL medium was used to calculate D_{out} . The values of 1.6×10^{-13} and $2.3 \times 10^{-13} \text{ m}^2\text{s}^{-1}$ were calculated for D_{in} using the discrete and continuous models, respectively. The value of $2.6 \times 10^{-13} \text{ m}^2\text{s}^{-1}$ was calculated for D_{out} using the discrete and continuous models. These values were calculated for the time period of 10 mins. to 40 mins. immersion.

Chromate Primer

The percentage mass loss, m_{loss} , as a function of $t^{0.5}$ for a 0.186 mm thick chromate primer is shown in Figure 4. There was an exponential decrease and an approach to an asymptotic value of 90%. This indicated that there was 10% saturation by water. The evolution of M_t/M_s with $t^{0.5}$ shown in Figure 4 indicated that the egress of water was consistent with Fick's second law. A D_{out} value of $3.3 \times 10^{-13} \text{ m}^2\text{s}^{-1}$ was calculated using Eq. (3) and the slope of the linear portion. This value was consistent with the value for an epoxy binder that is used for the house the chromate pigment in the chromate primer.

The evolution of the capacitance for the chromate primer panels during exposure to NaCl and RTIL media are shown in Figure 5. The capacitance increased for both panels during exposure to the NaCl medium. There was a decrease in capacitance on immersion in the RTIL for both panels with the capacitance recovering and increasing with time. The capacitance as a function of $t^{0.5}$ is shown in Figure 5 for P1 and P2 during the first immersion in NaCl from which it was observed that the change in capacitance was unlike that observed for the epoxy coating.

There was a decrease in capacitance associated with the immersion in RTIL for the epoxy coating as seen in Figure 1. This was not observed for the chromate primer upon immersion in RTIL. There was a decrease in capacitance for a short period of time, less than 10 minutes, followed by an increase in capacitance for P1 and P2. The reduction in capacitance would correspond to the removal of water, however the rate of this decrease would not be consistent with the diffusion coefficient that was calculated using gravimetric measurements. The observed increase in capacitance indicated that the dielectric property of the primer was increasing. A capacitance of 3 nF cm^{-2} for the 43 μm thick primer would yield a relative dielectric of approximately 150 for the primer assuming that the primer was a parallel plate capacitor. This in itself is anomalous, as the relative dielectric of water is approximately 80. It was inferred from these results that the RTIL was contributing to the large dielectric response and further experimentation is planned to determine the influence of RTIL on chromate pigmented primers. The effect of the RTIL was not reversed upon aqueous immersion suggesting that the cause of the larger dielectric response during the first wetting stages was compounded by the RTIL and not reversible. During the second wetting stages for P1 and P2, the calculated capacitance decreased initially upon immersion in NaCl but did not change significantly over the period of time monitored indicating that there was little water uptake.

The EIS data obtained at the end of the NaCl and RTIL exposures for panel P1 are shown in Figure 6. The Nyquist representation of the data indicated that there was a resistance component at low frequencies for both NaCl and RTIL immersions. This can be seen in the Bode modulus representation where a low frequency plateau region was observed for the NaCl immersion and a transition to a plateau was seen for the RTIL immersion. Two plateaus were observed for the NaCl immersion with the $|Z|$ value associated with the mid-frequency plateau being attributed to the bulk of the primer and the low frequency plateau attributed to the primer/metal interface. The resistance component observed for the RTIL exposure indicated was unlike the capacitance behavior of the epoxy. A possible explanation was that RTIL ionic species entered into the primer providing a measure of resistance.

In Figure 7, the value of the term associated with water uptake in Eq. (4) is shown as a function of time for the two panels during immersion in NaCl. The use of this term would indicate that there was a 50% uptake of water by volume. This was not plausible as such a large water uptake would be visually observable, and was not. This anomalous observation has been reported in literature before.²³

The discrete model dimensionless capacitance as a function of $t^{0.5}$ is shown in Figure 8 for the wetting and drying stages of P1 and P2. The evolution of the discrete model dimensionless capacitance was similar for the drying and wetting stages. It was observed that the time at which the dimensionless capacitance was unchanging was similar for the wetting stages of both panels and the drying stages of both panels. Comparison of capacitance changes of the epoxy shown in Figure 3 with the changes for the chromate primer shown in figure 8 indicated that the assumptions associated with the discrete model did not permit the calculation of a diffusion coefficient.

The dimensionless capacitance associated with the continuous model is given as functions of $t^{0.5}$ for the wetting and drying stages in Figure 8. It was observed that the wetting stages yield a capacitance evolution that was consistent with a linear increase with $t^{0.5}$ followed by an asymptotic approach to a steady value. The $t^{0.5}$ dependence suggested that a diffusion process was governing the change in capacitance. The calculated values for the assumed diffusion coefficient associated with the wetting stages were $5 \times 10^{-14} \text{ m}^2 \text{ s}^{-1}$ for both panels. This was calculated using the slope of the linear portion of the plot and Eq. (3).

The evolution of the capacitance for the chromate primer that was exposed to a wetting stage of NaCl immersion followed by a drying stage in a dessicator is shown in Figure 9. There was a capacitance increase during the first wetting stage that was dissimilar to that of the second wetting stage. The Bode modulus plots of the EIS spectra associated with the ends of the wetting stages are shown in Figure 9. The plots for the first and second wetting stages were similar for frequencies greater than 1 Hz. There was the transition to a low frequency plateau observed for the first stages while there was no indication of a low frequency plateau for the second stage. It was concluded from these results that there were no defects introduced between the stages. The continuous model dimensionless capacitance for the first and second stages yielded diffusion coefficient values of $5 \times 10^{-14} \text{ m}^2 \text{ s}^{-1}$ and $6 \times 10^{-13} \text{ m}^2 \text{ s}^{-1}$, respectively.

Hypothesis for anomalous behavior

The calculated value for the assumed diffusion coefficient associated with the wetting stages for the chromate primer of panels P1 and P2 was $5 \times 10^{-14} \text{ m}^2 \text{ s}^{-1}$, approximately an order of magnitude less than that calculated for the egress of water by gravimetric measurements, which was $3.3 \times 10^{-13} \text{ m}^2 \text{ s}^{-1}$. The observed water saturation for the primer from the gravimetric measurement was approximately 10%. A coating of 45 μm thick with a D value of $3.3 \times 10^{-13} \text{ m}^2 \text{ s}^{-1}$ and a saturation of 10 % would take approximately 24 hours to saturate. This was calculated using a finite difference model for Fick's second law. This was much less than the time for the chromate primers to attain an unchanging capacitance, which was 96 to 144 hours as seen in Figure 5.

The results presented were addressed by the following hypothesis. The gravimetric D value of $3.3 \times 10^{-14} \text{ m}^2 \text{ s}^{-1}$ was that of water ingress/egress in the primer. It would take about 48 hours for the primer to be saturated with water and based on Eq. (4), the dielectric change associated with 10% water saturation is only a factor of 1.6. The diffusion coefficient of ionic species in a coating was reported to be 10 times less than that of water in the coating. Therefore, the diffusion coefficient of $5 \times 10^{-14} \text{ m}^2 \text{ s}^{-1}$, was assumed to be that of an ionic specie in the electrolyte, Na^+ or Cl^- . The entry of this ionic specie was responsible for the large change in capacitance observed over the time period of 4 days.

The hypothesis presented is that the increase in capacitance of the chromate primers upon immersion in NaCl as seen in Figure 5 was due to the ingress of an electrolytic species. This hypothesis is supported by the data presented in Figure 9 that involves two wetting stages of 0.05 M NaCl

immersion with an intermediate dessicator drying stage. Upon the first exposure to a NaCl medium, there would be the diffusion of water into the primer until it is saturated with water and there would also be a slower diffusion of electrolytic species into the primer. The diffusion coefficient calculated for the first wetting stage, , was $5 \times 10^{-14} \text{ m}^2\text{s}^{-1}$, similar to that calculated for the first wetting stages of chromate primers P1 and P2. The drying process in the dessicator would remove only the water content with the electrolytic species remaining in the primer. The second wetting stage yielded a diffusion coefficient of $6 \times 10^{-13} \text{ m}^2\text{s}^{-1}$, using the continuous model, which was similar to that for the diffusion coefficient of water in the primer based on gravimetric measurements and the non-pigmented epoxy. The large increase in capacitance did not require the ingress of the electrolytic species as it was already there from the first wetting stage, but it did require the ingress of water. This hypothesis represents a work in progress upon which more sophisticated versions will be developed.

CONCLUSIONS

A non-pigmented epoxy coating yielded capacitance evolutions for water ingress during wetting and water egress during RTIL drying that were consistent with Fick's second law. The calculated diffusion coefficients for the wetting and drying processes demonstrated that the drying by RTIL was an adequate means of electrochemically monitoring the drying process. Gravimetric measurements for the chromate primer resulted in a diffusion coefficient of $3.3 \times 10^{-13} \text{ m}^2\text{s}^{-1}$ that was attributed to the water egress during the drying process. The capacitance evolution associated with the chromate primer was anomalous with a 50 factor increase in the capacitance during initial immersion in NaCl. This experimental result was addressed using the hypothesis that the large increase in capacitance of the chromate primers was due to the ingress of an electrolytic species. This hypothesis was supported by capacitance data presented for the primer exposed to two wetting stages of NaCl immersion with an intermediate dessicator drying stage. The influence of RTIL on a chromate primer that was previously immersed in a NaCl medium was not reversed upon further aqueous immersion suggesting that the cause of the larger dielectric response during the first immersion was compounded by the RTIL and not reversible.

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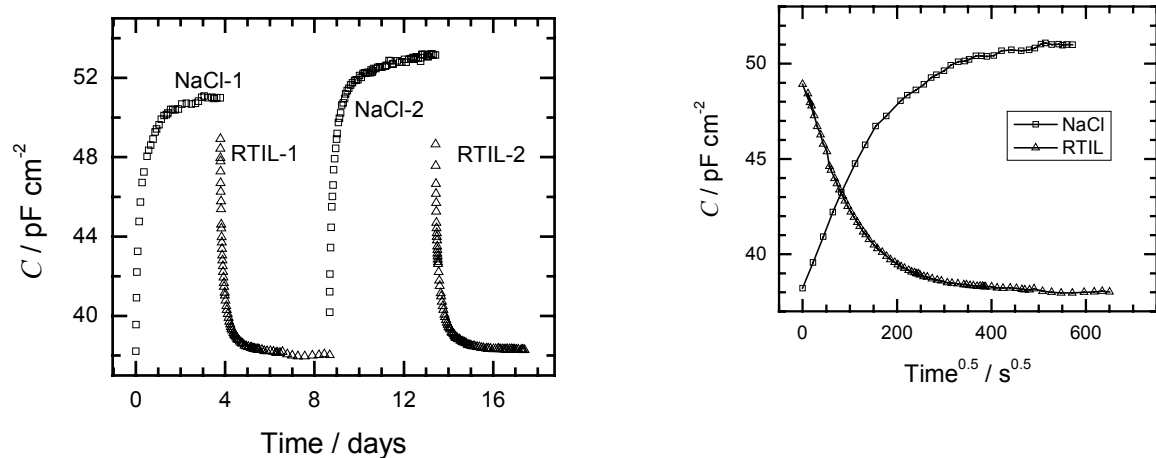


Figure 1. Calculated capacitance as a function of immersion time (left) and $t^{0.5}$ (right) during immersion of single-layer epoxy coating in NaCl and RTIL media.

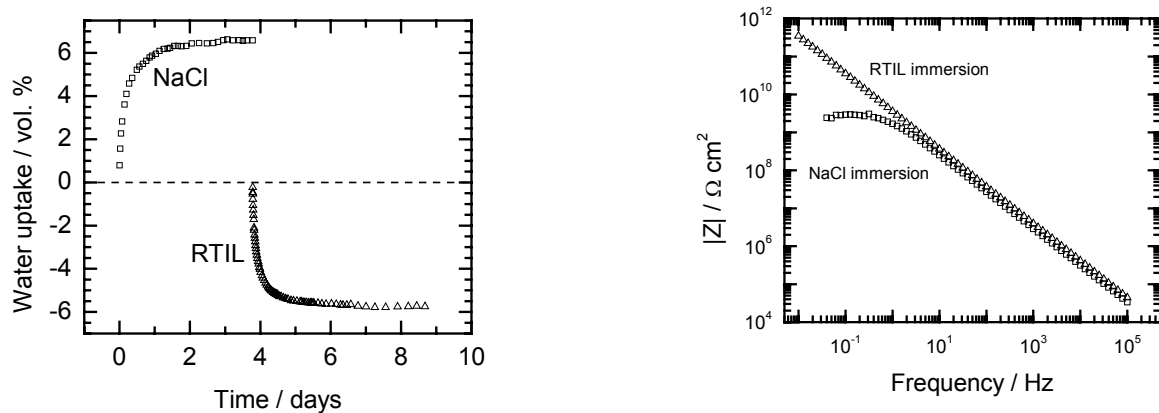


Figure 2. Water uptake evolution (left) and Bode modulus plot of EIS data (right) associated with the epoxy coating during the first immersions in 0.05 M NaCl and RTIL media. The EIS data was obtained at the ends of the wetting and drying stages.

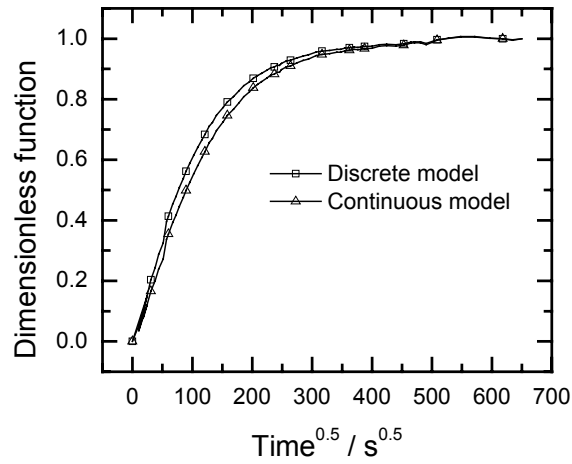


Figure 3. The values of the dimensionless functions associated with the discrete and continuous models as functions of $t^{0.5}$ calculated using the capacitance data obtained during immersion in NaCl and RTIL.

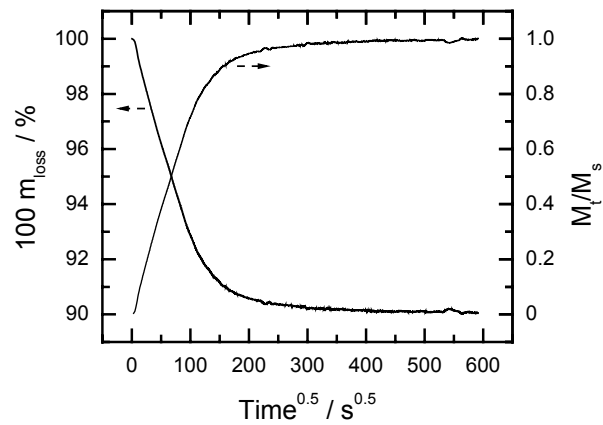


Figure 4. Percentage mass loss m_{loss} and degree of saturation M_t/M_s during the drying process in a TGA instrument.

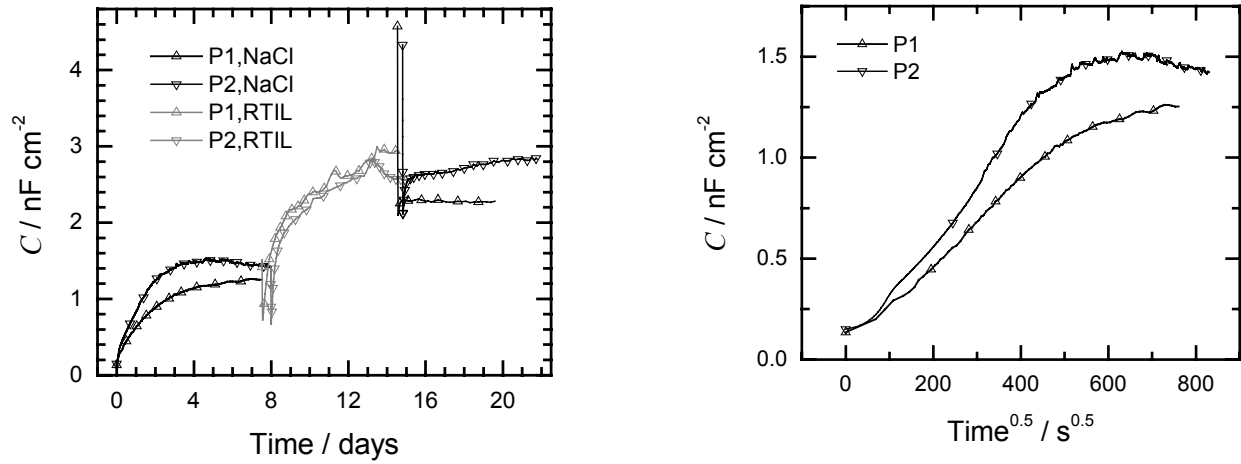


Figure 5. Calculated capacitance evolution for chromate primer panels during exposure to NaCl and RTIL media (left). Calculated water uptake evolution for the first immersion in NaCl for the chromate primer panels (right).

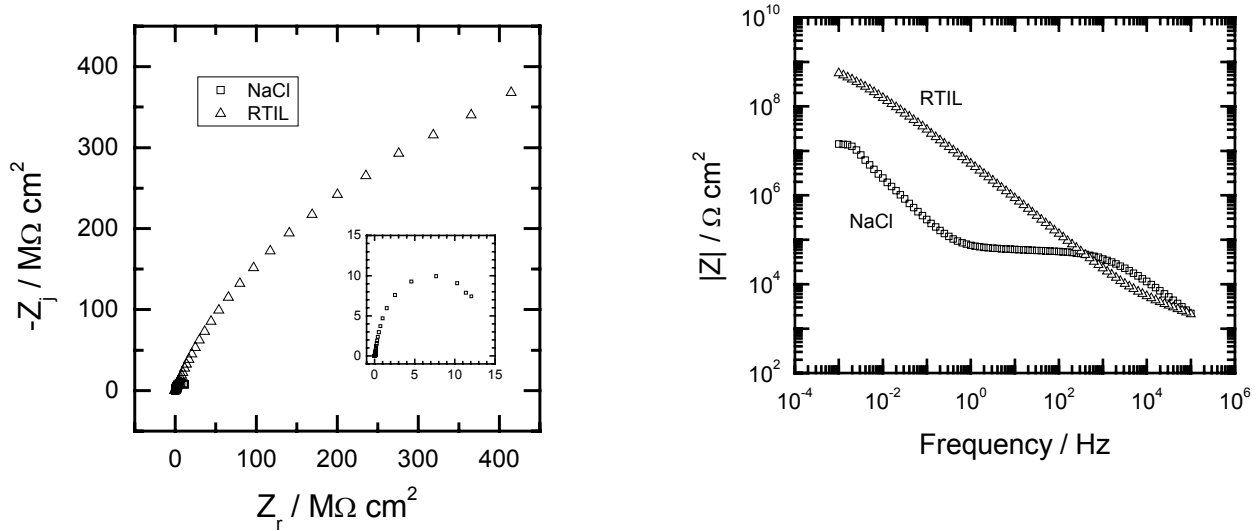


Figure 6. Nyquist (left) and Bode modulus plot (right) of EIS data associated with the first immersions of chromate primer P1 in NaCl and RTIL media.

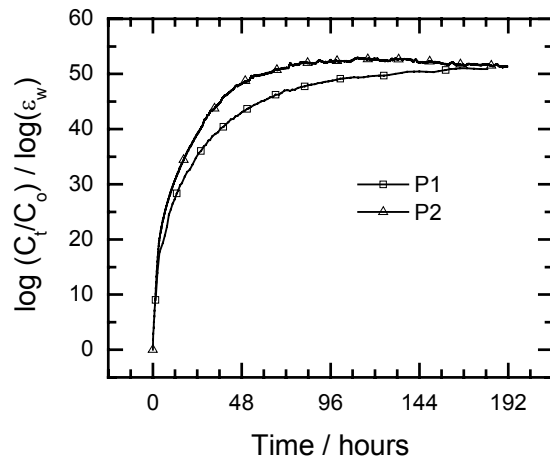


Figure 7. Evolution of calculated water uptake dimensionless function, Eq. (4), for the chromate primers during exposure to 0.05 M NaCl.

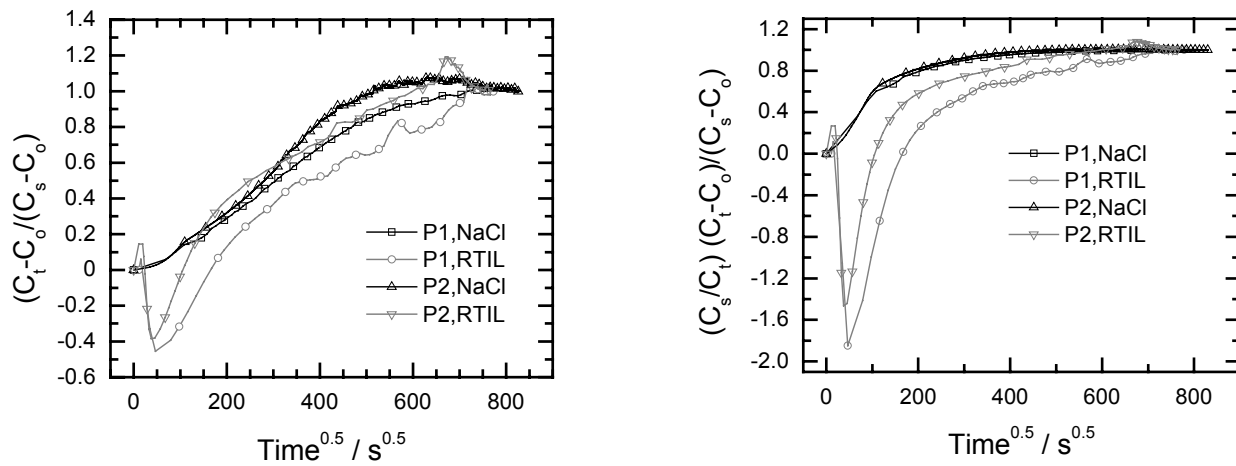


Figure 8. Calculated dimensionless functions for the discrete model (left) and continuous model (right) as functions of $t^{0.5}$ for the chromate primers in the first immersions of NaCl and RTIL media.

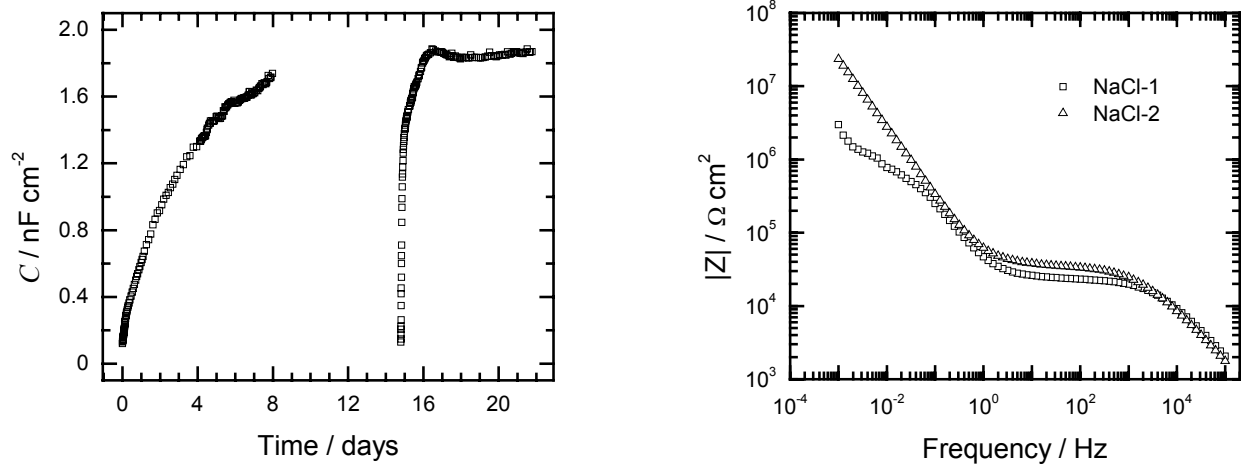


Figure 9. Calculated capacitance evolution (left) and Bode modulus plots for the EIS data associated with the ends of the wetting stages (right) for the chromate primer exposed to wetting in 0.05 M NaCl and drying in a dessicator.